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ATOMIC LAYER DEPOSITION FOR FABRICATING THIN FILMS

TECHNICAL FIELD OF THE INVENTION

The present invention generally relates to microelectronic device fabrication, and more particularly to atomic layer deposition for fabricating thin films.

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BACKGROUND OF THE INVENTION

Atomic layer deposition (ALD) has gained acceptance as a technique for depositing thin and yet continuous layers of metals and dielectrics with high conformality.

5 In ALD, a substrate is alternatively dosed with the precursor and one or more reactant gases so that reactions are limited to the wafer surface. Thus, gas phase reactions are avoided since the precursor and the reactant gases do not mix in the gas phase. Uniform
10 adsorption of precursors on the wafer surface during ALD produces highly conformal layers at both microscopic feature length scales and macroscopic wafer length scales, and achieves a high density of nucleation sites. These attributes result in the deposition of spatially
15 uniform, conformal, dense and continuous thin films.

The high quality films achievable by ALD have resulted in increased interest in ALD for the deposition of conformal barriers, high-k dielectrics, gate dielectrics, tunnel dielectrics and etch stop layers for
20 semiconductor devices. ALD films are also thermally stable and very uniform which makes them attractive for optical applications. Another potential application for ALD is the deposition of AlO_x as a gap layer for thin film heads, such as heads for recording densities of 50 Gb/in²
25 and beyond which require very thin and conformal gap layers. Conventionally sputtered gap layers are difficult to reliably scale below 300 Å due to excessive leakage currents. Although ion beam deposited gap layers can be scaled down in thickness to below 300 Å, such
30 layers tend not to be adequately conformal. Further, process integration considerations for thin film heads of

200 Å or less tend to constrain the maximum deposition temperature to below 200 °C.

Although ALD techniques support deposition of conformal thin layers, a number of difficulties exist which make commercial applications of ALD unworkable. One difficulty is that the repeated cycle of precursor and reactant adsorption and intervening chamber purges is time consuming, resulting in reduced throughput relative to conventional techniques. Another difficulty is that for a continuous monolayer of precursor to be adsorbed on the wafer without being thermally dissociated and for other process constraints, a relatively low deposition temperature is typically needed. However, the quality of the deposited thin film as measured by breakdown field strength tends to suffer at lower temperatures as impurities are incorporated in the film due to incomplete reaction of the precursor. Breakdown field strength comprises a good measure of film quality related to impurities, defects, roughness and film continuity.

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SUMMARY OF THE INVENTION

Therefore a need has arisen for a method and system which improves ALD thin film quality.

A further need has arisen for a method and system
5 which provides improved throughput for ALD thin films.

In accordance with the present invention, a method and system are provided that substantially eliminates or reduces disadvantages and problems associated with previously developed methods and systems for ALD.

10 Periodic annealing during ALD of thin films after a predetermined film thickness or associated number of deposition cycles improves film quality. Throughput is improved by maintaining desired process parameters for precursor flow, reactant flow and purge cycles, with
15 reduced cycle time and risk of introducing impurities accomplished with a dual zone showerhead to limit mixing of residual reactants.

More specifically, a method of fabricating a conformal thin film for integrated electronic structures
20 is provided. ALD cycles of adsorbing and reacting a precursor on a wafer to deposit the thin film are performed with intervening anneals to control the quality of the ALD film. Process throughput and quality are enhanced by the use of a dual zone showerhead and by
25 control of predetermined process parameters, such as precursor and reactant flow times and quantity, purge times, the number and frequency of anneals, and wafer temperature, so that contaminants are reduced and film breakdown field strength and intrinsic stress are at
30 desired levels.

In one embodiment of the present invention, an aluminum oxide thin film is deposited with a predetermined number of ALD cycles and with one or more intervening anneals performed after a predetermined number of ALD cycles or associated number film thickness. An ALD cycle comprises distributing a precursor through a first zone of a multi-zone shower head to achieve a continuous monolayer of precursor adsorption on the wafer, and purging the processing chamber. The monolayer of precursor is oxidized with a flow of water through a second zone of the multi-zone showerhead, and the processing chamber purged to prepare for another ALD cycle. The wafer is maintained at a generally low temperature of between 60 and 350 C to aid in the adsorption of a continuous monolayer of precursor that is not thermally dissociated. Every 25-50 Å of film thickness, which at .8Å per ALD cycle takes approximately 25 to 50 ALD cycles, a thermal or plasma anneal of the ALD film is performed in a reactive ambient to reduce impurity incorporation that generally results from lower wafer temperatures that leave the chemical reaction between the precursor and reaction gas incomplete. For instance, by varying the frequency of an in-situ RF plasma anneal in an Ar/O₂ ambient, the intrinsic film stress of the AlO_x film can be varied from tensile to compressive. The use of the multi-zone showerhead, predetermined precursor and reactant pulse times, and adequate purging increases throughput and reduces the introduction of contaminants to the wafer.

According to a further aspect of the invention, a microstructure having a thin film deposited using an

atomic layer deposition (ALD) is disclosed. The microstructure includes a substrate having a thin film fabricated using a low temperature atomic layer deposition wherein the thin film includes at least one
5 plasma annealed layer.

The present invention provides a number of important technical advantages. One important technical advantage is that intrinsic stress is varied from tensile to compressive and breakdown voltage for an ALD film is
10 enhanced by varying the number of plasma anneals performed for a predetermined number of ALD cycles. For instance, a 60 - 200 °C atomic layer deposition (ALD) process that provides smooth ($R_a \sim 2\text{\AA}$), pure (impurities < 1 at. %), and highly conformal (100% step coverage) AlO_x
15 films with excellent breakdown strength (9 - 10 MV/cm) is provided by performing a plasma anneal every 25 to 50 ALD cycles. In one form, optimal chamber configuration and precursor / oxidant delivery methods have been identified for trimethylaluminum (TMA) as an aluminum source and
20 water as an oxidant.

Another important technical advantage is that the resulting ALD AlO_x films are conformal and exhibit excellent insulating characteristics down to 5 - 10 Å to support thin film applications such as a gap layer for
25 thin film heads or a tunnel barrier for magnetic tunnel junctions. Plasma annealing the films in-situ every 25 - 50 Å, makes the as-deposited tensile stress slightly compressive and the breakdown field to exceed 10 MV/cm. Advanced thin film heads for recording densities of 50
30 Gb/in² and beyond require very thin and conformal gap layers. The process uses trimethylaluminum (TMA) as the

aluminum source and water as the oxidant. Although ALD provides a relatively low deposition rate, with proper chamber design, commercial production throughput requirements can be met despite a relatively low
5 deposition rate of approximately 0.8 to 1.1 Å/cycle. A small chamber volume that allows a cycle time of 5 s meets production throughput requirements of 4 - 6 wph for a 100 Å film.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the present embodiments and advantages thereof may be acquired by referring to the following description taken in
5 conjunction with the accompanying drawings, in which like reference numbers indicate like features, and wherein:

FIGURE 1 illustrates a flow diagram of a low temperature ALD process for fabricating thin films according to one aspect of the invention;

10 FIGURE 2 illustrates a system operable to employ a low temperature ALD process for fabricating thin films according to one embodiment of the invention;

FIGURE 3 illustrates a cross section view of a thin film magnetic read/write head incorporating low
15 temperature ALD thin films according to one aspect of the invention;

FIGURE 4 is a graphic illustration of a simulation for determining mole fractions of a precursor and an oxidant within a process chamber during an ALD process
20 sequence according to one embodiment of the invention;

FIGURE 5 is a graphic illustration of an I-V curve as a function of inlet precursor flow at a deposition temperature of 350 °C for approximately 200 Å ALD AlO_x according to one embodiment of the invention;

25 FIGURE 6 is a graphic illustration of an I-E curve as a function of TMA precursor flow time at a deposition temperature of 200 °C for approximately 250 Å ALD AlO_x and 10 Å ALD AlO_x according to one aspect of the invention;

FIGURE 7 is a graphic illustration of an I-E curve as a function of deposition temperature for approximately 275 Å ALD AlO_x according to one aspect of the invention;

FIGURE 8A is a graphic illustration of one
5 embodiment of an I-E curve as a function of ALD O_x thickness for films deposited at 200 °C on a silicon substrate according to one aspect of the invention;

FIGURE 8B is a graphic illustration of one
10 embodiment of an I-E curve as function of ALD AlO_x thickness for films deposited at 200 °C on a silicon substrate having a 50 Å layer of tantalum according to one aspect of the invention;

FIGURE 9 is a graphic illustration of film stress as
15 a function of plasma annealing for approximately 300 Å ALD AlO_x according to one aspect of the invention;

FIGURE 10 is a graphic illustration of I-E curves as
a function of plasma annealing for approximately 300 Å
ALD AlO_x according to one aspect of the invention;

FIGURE 11A is a graphic illustration of ALD AlO_x
20 deposited at 350 °C on a silicon substrate with a normalized precursor flow of 4 sccm according to one aspect of the invention; and

FIGURE 11B is a graphic illustration of ALD AlO_x
deposited at 200 °C on tantalum with a normalized
25 precursor flow of 25 sccm according to one aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Preferred embodiments and their advantages are best understood by reference to FIGURES 1 through 11, wherein like numbers are used to indicate like and corresponding
5 parts.

The conceptual groundwork for the present invention involves a low temperature atomic layer deposition (ALD) processes to create highly conformal thin films. In one form, a substrate is hydroxylated and a precursor
10 introduced to the substrate within a low temperature ambient resulting in an atomic layer deposition thin film of AlO_x having minimal impurities and a thickness of approximately 0.8 \AA per deposition cycle. During the process, one or more ALD layers are annealed to provide a
15 slightly compressive film that enhances the film's breakdown voltage. For instance, in-situ plasma annealing in an Ar/O_2 ambient every 25 to 50 \AA of deposition thickness enhances an AlO_x thin films breakdown strength and allows fine tuning for another degree of
20 freedom for film stress control.

One important application for AlO_x thin films deposited according to the present invention is in giant magnetoresistive recording heads. For instance, film stress control in such recording heads is important for
25 stabilizing the bias point or the operation point to ensure sufficient read sensor output amplitude. An advantage of the present invention is that additional degree of freedom for film stress control associated with varying the frequency of in-situ plasma annealing
30 improves giant magnetoresistive recording head quality. In addition, during the recording head integration

process, deposition temperature is an important factor. For instance, photoresist patterns and sensor thermal stability during the integration process generally require process temperatures of below 200 to 230 °C to
5 prevent photoresist from flowing and atomic interdiffusion in the multilayer thin films. The present invention supports deposition of AlO_x thin films in the temperature range of 60 to 200 °C with superior structure integrity, physical properties and topographic
10 conformality.

FIGURE 1 illustrates an ALD process based on sequentially dosing a substrate with an aluminum bearing precursor and an oxidant. In one embodiment, trimethylaluminum (TMA), a highly volatile precursor with
15 a vapor pressure of 11 Torr at room temperature, may be used as an aluminum source. Trimethylaluminum is thermally stable at temperatures less than 350 °C ensuring that the precursor remains intact when chemisorbed on substrate 101 until it reacts with an
20 oxidant. Trimethylaluminum is a pyrophoric liquid at room temperature and is diluted to a 10% weight in octane or similarly effective dilutions to make the trimethylaluminum less pyrophoric. In other embodiments, precursors such as tri-isobutylaluminum (TIBA) and
25 dimethylaluminum hydride (DMAH), although sufficiently volatile, may be used giving regard to thermal decomposition at temperatures as low as 200 °C. Halogenated precursors such as AlCl_3 may also be used, but
30 may also result in ~ 0.5% chlorine incorporation. Organometallic precursors may incorporate trace amounts

of carbon and hydrogen but these are usually benign and may not deteriorate film properties. Other embodiments may include using oxygen bearing aluminum precursors, but these are generally hydrophobic and may not readily
5 chemisorb on hydroxylated (i.e. OH containing) surfaces.

The process illustrated in FIGURE 1 begins at step 100 with a surface hydroxylation of substrate 101 using water as an oxidant resulting in OH groups chemisorbed on the surface of substrate 101 heated to a temperature of
10 approximately 150 °C - 200 °C, although a temperature range of between 60 °C - 350 °C will prove operable. Surface hydroxylation helps to drive the chemisorption of subsequent TMA molecules, although adsorption of TMA may be performed followed by surface hydroxylation. Upon
15 hydroxylating the surface of substrate 101, a chamber housing substrate 101 may be purged 102 and subsequently a precursor, such as TMA, may be introduced 103 into the chamber and chemisorbed to the hydroxylated surface of substrate 101. The method then proceeds to step 104
20 where an inert gas is introduced to the chamber to purge the remaining precursor from the chamber. Upon purging the chamber the method proceeds to step 105 where the method determines if substrate 101 having an ALD layer should be annealed 105. If substrate 101 should be
25 annealed the method proceeds to step 106 to anneal substrate 101 and to step 107 to determine if a desired thickness has been achieved. The method then repeats until a desired film thickness is achieved or to step 105 where the method ends. As a result, a substantially
30 continuous monolayer of precursor deposits a thin film on the surface of substrate 101.

Through chemisorption, the process ensures that the precursor is not desorbed from substrate 101 during purge step 104 thereby reducing precursor concentration in the gas phase to trace levels before introduction of an oxidant. Alternate embodiments may include using a variety of oxidants (e.g. H_2O_2 , O_2 , O_3 , N_2O , etc.), however H_2O appears to be well-suited for the aforementioned reasons. Additionally, a different reagent gas (e.g. NH_3) may be used for ALD AlN and ALD AlO_xN_y . For example, crystalline AlN films can be deposited at $300\text{ }^\circ\text{C}$ - $400\text{ }^\circ\text{C}$ and 25 - 50 Torr using alternating pulses of DMEAA and NH_3 .

In another embodiment, a process cycle for FIGURE 1 may include depositing an ALD layer using heating of substrate 101 at a desired temperature (e.g., $200\text{ }^\circ\text{C}$ - $350\text{ }^\circ\text{C}$) in an inert ambient at a process pressure. Substrate 101 may then be dosed with oxidant (H_2O) to hydroxylate the surface of substrate 101. The oxidant may be transported using a carrier gas. The process chamber may then be purged with a high flow of inert gas to reduce water concentration in the delivery line, showerhead and chamber to trace levels. Substrate 101 may then be dosed 103 with a short pulse (0.5 s - 2 s) of precursor to adsorb a continuous monolayer of precursor on the surface of substrate 101. The precursor may be transported to substrate 101 by a carrier gas while maintaining chamber pressure at its set-point value. The chamber may then be purged 104 with a high flow of inert gas to reduce precursor concentration in the delivery line, showerhead and chamber to trace levels. The process may then be repeated multiple times to obtain a

desired film thickness. For example, each cycle may deposit $\sim 0.8 \text{ \AA}$ of AlO_x on substrate 101.

The method of FIGURE 1 advantageously provides a continuous monolayer of precursor adsorbed on substrate 101 that is not thermally dissociated using a low deposition temperature. At lower temperatures, a chemical maintained reaction between precursor and reacting gas may not go to completion resulting in impurity incorporation. In one form, impurity incorporation may be reduced by annealing one or more layers in a reactive ambient every 25 - 50 \AA of deposition. Annealing 106 may include either a thermal (RTP) anneal or a plasma anneal and may be used periodically to reduce film stress of the resulting ALD layers. RTP cycle utilizes a lamp and elevated temperatures and may not be desired for all embodiments. A lower relative processing temperature may be achieved by employing an in-situ plasma anneal in an Ar / O_2 ambient to ensure complete oxidation and controlling film stress. As such, the method of FIGURE 1 may incorporate an optional in-situ plasma annealing step in an Ar / O_2 ambient periodically (e.g. every 25 - 50 \AA or approximately every 25-50 ALD cycles) at the termination of an ALD cycle. By altering the frequency of anneals, intrinsic film stress can be varied from tensile to compressive and breakdown voltage can be enhanced.

FIGURE 2 illustrates a system operable to employ a low temperature ALD process for fabricating thin films according to one embodiment of the invention. A process system, illustrated generally at 200, may be optimized for an ALD process according to teachings of the

invention and may include a Veeco Nexus 800 cluster tool equipped with a module for sputter etch, and a CVD module optimized for ALD and configured to process 200 mm substrates. System 200 includes a warm-wall stainless steel chamber 201 with wall temperature regulated at approximately 70 °C. Reactants may be introduced through a multi-zone showerhead 203 maintained at approximately 100 °C. A two-zone resistively heated chuck 204 with a backside Ar gas flow 207 and substrate clamping ensures good thermal contact and uniform wafer temperature. A turbo molecular pump 220 may be used to achieve good base pressure while a dry pump may be used to pump the process gases during the process. Chamber 201 may be pumped down to 10⁻⁶ Torr prior to deposition using turbo molecular pump 220.

A trimethylaluminum source 215 with a vapor pressure of 11 Torr at room temperature may be used as a precursor source. High vapor pressure provides sufficient pressure differential to achieve a high flow of TMA into chamber 201 that is in the Torr range. An Ar carrier gas 214 sweeps the precursor into the chamber through first showerhead zone 203A. During the TMA purge step, the TMA flow is shut off and the Ar flow is increased substantially to purge chamber 201 through first showerhead zone 203A. Ar 217 may be bubbled through a room temperature water bubbler 211 at regulated pressure to transport water into the chamber through second showerhead zone 203B. Additional diluent Ar 213 may be fed into second showerhead zone 203B. At the conclusion of the water flow step, a high Ar flow through second showerhead zone 203B purges chamber 201. The use of a

dual showerhead limits mixing of residual reactants which could otherwise introduce impurities to the chamber. An Ar purge 207 introduced through the base of chamber 201 acts as a ballast gas load to help regulate chamber
5 pressure. The substrate is clamped to heated chuck 204 with backside Ar to enhance heat transfer. Chuck 204 is RF biased 208 for a plasma anneal cycle as desired, such as every 25 to 50 TMA/H₂O ALD cycle. An Ar/O₂ mixture 205 is fed through the MESA valve port 207 during the plasma
10 anneal step.

Several constraints apply to flow rates and durations for each of step in an ALD sequence and should be considered to achieve the desired film quality. Each step should be substantially short to decrease the
15 duration of each cycle and enhance the effective deposition rate. For example, with a deposition rate of 0.8 Å/cycle and a cycle duration of 20 s, the effective deposition rate is ~ 2.5 Å/min. Reducing the duration of the cycle to 5 s increases the effective deposition rate
20 to ~ 10 Å/min. Since typical film thickness for some gap applications is 150 Å, the substrate throughput may be significantly affected by the effective deposition rate that can be achieved by system 200. Given that a short step time is desirable, system 200 may be configured such
25 that response time of components associated with gas and precursor delivery be substantially shorter than the step time.

For example, step time should exceed by a factor of 3X - 5X, the time required to deliver the gas and/or the
30 precursor from the shutoff valve 221 into chamber 201. Transit time may be estimated as: $t_s = VP / QP_0$ where V

is the volume of the delivery line / showerhead
downstream of shutoff valve (CM^3) 221, Q is the flow rate
of the carrier gas (scc/s), P is the operating pressure
(Torr) and $P_0 = 760$ Torr. Short delivery lines, high
5 carrier flows and connective transport to the substrate
may shorten transit time. As such, transit time may be
reduced to a fraction of second.

During the ALD process, a continuous monolayer of
precursor adsorption on the substrate is desirable. For
10 a continuous monolayer coverage precursor concentration
in the gas phase must exceed a threshold value to
saturate all of the adsorption sites on the substrate.
For example, during a Langmuir adsorption processes the
fractional coverage increases linearly with precursor
15 partial pressure initially and levels off to 100% once a
threshold pressure has been exceeded. Threshold pressure
may be determined experimentally from deposition rates
and film properties. Additionally, precursor
concentration should not greatly exceed the threshold
20 value due to the excess precursor adsorbs on chamber 201
walls and negatively impacting precursor utilization.
Chemisorption occurs on time-scales of tens of
milliseconds so the shortest pulse time that is
controllable and meets the other criteria should be used.
25 For example, longer pulse times tend to waste precursor
and increase total duration of a cycle. As such, the
total amount of precursor delivered should exceed the
quantity adsorbed on the wafer by a factor of 50X - 500X
to account for precursor consumption (adsorption) on the
30 chamber walls.

Another process consideration includes providing substantially lower water flow compared to TMA flow to oxidize a monolayer of TMA since the TMA is very water sensitive. For example, the total quantity of water delivered should exceed the amount required to convert the TMA adsorbed on the substrate by a factor of 2X - 5X. In some embodiments, water tends to adsorb on chamber 201 walls. As such, water flow should be as minimal as possible compared with excess TMA due to excess TMA reacting with residual water on chamber 201 walls. Water flow rate and pulse time should be sufficient to substantially hydroxylate the substrate surface and achieve the maximum deposition rate per cycle, but so that the flow duration has minimal effect on film properties.

During processing, purge flow rates should be sufficiently high to reduce precursor and oxidant concentrations to trace levels after each respective step. For example, if a purge is insufficient, residual precursor concentration in the gas phase will be too high and gas phase reactions that form alumina particles may result when oxidant is introduced. Similarly, care should be taken to ensure that precursor and oxidant never co-flow into chamber 201, into a common delivery line, or into the exhaust to avoid alumina powder formation. As such, system 200 incorporates a liquid delivery system architecture in which the precursor flow is diverted into an exhaust line while an oxidant is flowing (or vice versa) is not possible, since the two would mix in the exhaust line.

System 200 advantageously provide a small relative chamber volume that may be purged more effectively and as such is desirable for ALD applications. Utilizing plasma anneal 208 limits the minimum chamber volume that can be realistically achieved and should be considered.

FIGURE 3 illustrates a cross section view of a thin film head incorporating low temperature ALD thin films according to one aspect of the invention.

A magnetic thin film head, illustrated generally at 300, includes a magnetic read sensor 320 and an inductive write element 321 having one or more thin films fabricated using a low-temperature ALD process. A substrate 302 includes a bottom shield 303 coupled to an interlayer 306 of Cr-Co-Pt. Interlayer 306 couples contacts 307 to bottom shield 303. Contacts 307 include Ta-Mo-Au-Cr materials coupled to a top read gap layer 308. Lower polysilicon layer 309 provides a top shield between top read gap layer 308 and top write gap layer 311. An upper polysilicon film 312 is coupled to a thin layer 311 operable as coils, leads and/or studs for inductive write element 321. Upper polysilicon layer 312 may include FeTaN-NiFe-CoFe materials within inductive write element 321. An overcoat 313 protects inductive write element 321.

FIGURES 4 - 11 illustrate data for process variation of the method illustrated in FIGURE 1 using system 200 of FIGURE 2. System 200 and the method of FIGURE 1 are illustrative of one embodiment for providing low-temperature ALD processes. As such, other systems or methods may be used within the scope and teachings of the present invention.

FIGURE 4 is a graphic illustration of a simulation for determining mole fractions of a precursor and an oxidant within a process chamber during an ALD process sequence according to one embodiment of the invention. A gas flow simulation is useful to confirm that precursor, water delivery and purge steps are effective in attaining the desired concentrations at the surface of a substrate. Cycling of precursor and water concentrations in a chamber during various steps (precursor dosing, purge, water dosing, purge) such as the method in FIGURE 1 using system 200 of FIGURE 2 can be simulated using the formula:

$$X_{n+1} = (X_i - X_n) \exp[-QP_0(t_{n+1} - t_n)/VP] + X_n$$

where X_{n+1} is the mole fraction at time t_{n+1} , X_n is the concentration at time t_n , X_i is the inlet concentration of the species of interest, Q is the total flow rate (scc/s), P is the chamber pressure (Torr), V is the chamber volume (cm^3) and $P_0 = 760$ Torr. For the process conditions described above, variation of TMA and water mole fractions at the end of precursor dosing, first purge, water dosing, and second purge steps are shown in FIGURE 4. Note that the same steady state concentrations of precursor and water are achieved during each cycle because the purge steps are effective in reducing the residual concentrations to near zero levels.

FIGURE 5 is a graphic illustration of an I-V curve as a function of inlet precursor flow at a deposition temperature of 350 °C for approximately 200 Å ALD AlO_x according to one embodiment of the invention. Breakdown field strength is a good measure of film quality since impurities, defects, roughness and lack of film

continuity compromise breakdown strength. FIGURE 5 illustrates breakdown field strengths for films deposited on 200 mm bare p-type Si substrates with a resistivity of 1 - 10 Ω .cm. In some cases, the substrates were
5 subjected to a 20 s sputter etch to remove ~ 20 Å of native oxide. However, breakdown fields with and without a sputter etch were similar, indicating that the native oxide and any increase in surface roughness due to sputter etching has minimal impact on the breakdown
10 strength. As such, breakdown strengths are also measured on bare Si substrates without ALD AlO_x.

Breakdown field increases monotonically from zero as the precursor flow rate (Q_{TMA}) into the chamber increases. At the lowest precursor flow rate the breakdown field
15 strength is ~ 3 MV/cm (@ 0.01 A/cm²). The I-V curves of FIGURE 6 illustrate that the breakdown strength increases to 9 MV/cm at a precursor flow rate that is 25 times higher. FIGURE 6 is a graphic illustration of an I-E curve as a function of TMA precursor flow time at a
20 deposition temperature of 200 °C for approximately 250 Å ALD AlO_x and 10 Å ALD AlO_x according to one aspect of the invention. As the inlet concentration of precursor is above a threshold value, increasing the precursor flow duration from one second to two seconds does not affect
25 the breakdown strength or the deposition rate significantly. For example, the deposition rate increases from 0.83 Å/cycle to 0.89 Å/cycle while the breakdown field strength increases slightly. Once a sufficient precursor dose has been achieved, the growth
30 rate should not change.

Additionally, flow duration of 1 s may be too short compared to the transit time of the precursor from the delivery valve to the substrate. For example, I-V curves illustrated in FIGURE 6 include ultra-thin films (10A) deposited with one second and two second long precursor flow pulses. The longer flow time ensures that film growth is continuous from the very first layer. For example, when the TMA flow duration was reduced from two seconds to one second, the breakdown strength of the films decreased from 10 MV/cm to 6 MV/cm. Further, the order of steps of the process (i.e. whether TMA is introduced first or the water is introduced first) does not affect the breakdown strength of the resulting ALD layer.

FIGURE 7 is a graphic illustration of an I-E curve as a function of deposition temperature for approximately 275 Å ALD AlO_x according to one aspect of the invention. The I-E curves illustrated in FIGURE 5 show that the breakdown field is relatively invariant with deposition temperature in the range of 150 - 350 °C indicating the temperature window for a low temperature ALD process is relatively wide. An increase in deposition temperature accompanied by a gradual decrease in deposition rate from ~ 0.85 Å/cycle at 200 °C to 0.6 Å/cycle at 350 °C, resulting in a slight decrease in breakdown field strength. The low electric field characteristics are similar over this temperature range and optimal breakdown properties may be obtained in the temperature range of 175 °C - 200 °C.

FIGURES 8A and 8B illustrate I-E curves as a function of ALD AlO_x film thickness. The dependence of

breakdown voltage on film thickness shows a linear trend for films as thin as 5 and 10 Å indicating that a continuous layer-by-layer growth may be achieved using low temperature ALD processes. Additionally, native
5 oxide if present does not affect the breakdown strength. FIGURES 8A and 8B illustrate that leakage current remains low until failure occurs with a sharp increase in leakage current. As such, the low temperature ALD process results in excellent insulating characteristics of ALD
10 AlO_x even at 5 and 10 Å make it a candidate for tunnel barrier applications. FIGURES 8A and 8B also show that the breakdown field strength gradually increases as the thickness increases from 5 Å to 25 Å, but then declines slightly for thicker films. This behavior is consistent
15 with observations for thermal SiO₂. Also leakage currents at lower fields are higher for the thinner films due to the contribution of tunneling currents. Breakdown fields are similar on both Si and Ta confirming that the native oxide has minimal effect on the breakdown strength of the
20 ALD film.

FIGURE 9 is a graphic illustration of film stress as a function of plasma annealing for approximately 300 Å ALD AlO_x according to one aspect of the invention. Most ALD AlO_x films have a low tensile stress as-deposited,
25 ranging from 150 MPa at 200 °C to over 500 MPa at 150 °C. In general, low compressive stress is favored for dielectric films. In order to make the stress compressive, the lower temperature ALD process may include an in-situ plasma anneal every 25 - 50 Å of
30 growth. Plasma annealing makes the film compressive and a low (< 200 MPa) compressive can be obtained. As

illustrated in FIGURE 9, the film thickness is not significantly affected indicating the absence of deposition and any significant etching during the annealing step. FIGURE 10 is a graphic illustration of I-E curves as a function of plasma annealing for approximately 300 Å ALD AlO_x according to one aspect of the invention. Plasma annealing increases the breakdown strength of the ALD AlO_x thin film.

There is a correlation between ALD AlO_x roughness and the breakdown field strengths. For films deposited at 200 °C with an adequate flow of precursor (normalized flow = 25), the breakdown field strength is ~ 10 MV/cm and the films are very smooth with R_a ~ 2 Å. In comparison, films deposited at lower precursor flows (relative flow = 4) have a lower breakdown strength of ~ 6 MV/cm and are substantially more rough with R_a ~ 5 Å. Low roughness of the films illustrates the growth is monolayer by monolayer rather than island type growth that is typical of most CVD processes. For island type growth, the film roughness increases with film thickness while it is relatively invariant with thickness for the ALD growth mode. Another measure of film continuity is pinhole density. To measure the pinhole density, 100 - 200 Å films were deposited on NiFe and subjected to an acid dip to decorate the pinholes. No pinholes were observed in a 10X field of view in an optical microscope. The wet etch-rate in photo-resist developer is similar to that for ion beam deposited alumina confirming the chemical stability of this material.

FIGURE 11A is a graphic illustration of ALD AlO_x deposited at 350 °C on a silicon substrate with a

normalized precursor flow of 4 sccm according to one aspect of the invention. The CH_3 groups are removed entirely from the ALD AlO_x by using H_2O as the oxidant since the [C] content in the films is at the detectable limits of Auger analysis. The films are stoichiometric within the resolution of Auger analysis as illustrated in FIGURES 11A and 11B even at deposition temperatures as low as 200 °C. Additionally, [H] content is ~ 5%. The changing [H] content may cause the refractive index to increase from 1.64 to 1.68 as the deposition temperature increases from 250 °C to 400 °C.

One primary advantage of low-temperature ALD AlO_x is step coverage that may be achieved. Substantially conformal deposition (100% step coverage) can be obtained even in very aggressive structures having small geometries. Unlike PVD films, the dielectric properties are expected to be similar in the field and the sidewall. For PVD films, dielectric properties are usually worse on the sidewall in addition to poor step coverage because of self-shadowing effects.

Deposition rate is weakly dependent on temperature, which translates to very good deposition uniformities compared to most CVD processes. A deposition uniformity and repeatability of ~ 1% can easily be achieved. Properties of ALD AlO_x deposited at 200 °C under optimal process conditions may include a thin film thickness between 100-300 Å, a deposition rate of ~ 0.85Å/cycle, a refractive index of 1.64-1.65, compressive stress of less than 200 MPa, roughness (200 Å) of less than 2 Å, stoichiometric composition, impurities of less than 1%, amorphous morphology, a density (g/cm^3) of 3.65 (92% of

bulk), a breakdown field of > 10 MV/cm, and leakage current (A/cm^2) of $< 10^{-8}$ @ 1 MV/cm.

In one embodiment, the following parameters deposit a desirable film:

Parameter	H eat	W ater	P urge	T MA	P urge	ost
Step	1	2	3	4	5	
TMA (sccm)				25		
Octane (sccm)				300		
Water (sccm)		0 .54				
Ar carrier 2 (sccm)		63				
Bubbler (psig)	35	35	35	35	3	5
Diluent Ar 2 (sccm)	200	200	200	200	2 00	00
Ar Carrier/Purge 1 (slm)	0 .05	0 .05	0 .05	0 .05	2	
Ar Purge 2 (slm)			2			
Ar Bottom (slm)	2	2	2	2	2	
Pressure (Torr)	3	3	3	3	3	
Chuck Z1 ($^{\circ}C$)	214	214	214	214	2 14	14

Parameter	H eat	W ater	P urge	T MA	P urge	ost
Chuck Z2 (°C)	263	263	263	263	2 63	63
Wafer (°C)	200	200	200	200	2 00	00
Time	180	2	9	2	5	

Steps 2-5 represent a single ALD cycle and are repeated multiple times to deposit a film of desired thickness, with a film of approximately .85 Angstroms deposited each cycle. At every 25 to 50 Angstroms of thickness, an in-situ plasma anneal is performed. Step 6 represents a sequence of three pump and purge cycles performed upon completion of the film. These parameters provide a high quality film, however, modifications to these parameters, including the frequency of plasma anneals, are possible to achieve a desired breakdown strength and film stress.

Although the disclosed embodiments have been described in detail, it should be understood that various changes, substitutions and alterations can be made to the embodiments without departing from their spirit and scope.